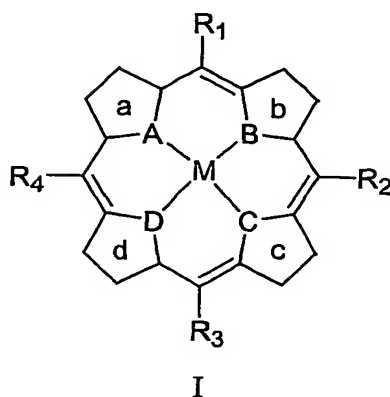


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CLAIMS

1. A compound of formula I, or a pharmaceutically acceptable salt thereof,



wherein

one or two of A, B, C and D are each independently selected from S, O, Se and Te, and the remainder are N;

a, b, c and d are each independently substituted or unsubstituted 5-membered heterocyclic groups having the members necessary to complete a porphyrin, chlorin, bacteriochlorin or isobacteriochlorin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te;

M is H or a metal;

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each independently selected from:

H;

alkyl;

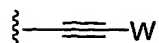
cycloalkyl;

halogen;

aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, COOH, COO-alkyl, -OZ, -COOZ, a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative,

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$-\text{C}\equiv\text{C}-(\text{CH}_2)_p\text{CO}_2\text{R}_{10}$ , where  $\text{R}_{10}$  is H or alkyl, and  $\text{O}(\text{CH}_2)_r\text{COR}_{11}$ , where  $\text{R}_{11}$  is OH, O-alkyl or N-succinimide, and  $p$  and  $r$  are each independently an integer from 1 to 10;



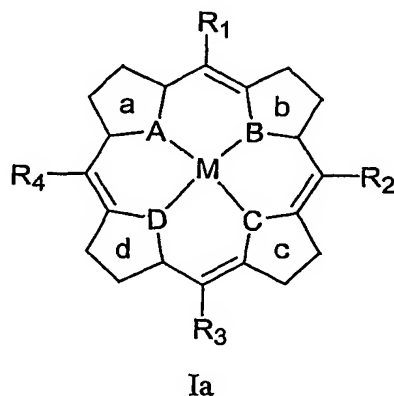
wherein  $W$  is an aryl, alkyl or heteroaryl group, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $\text{CF}_3$ , alkyl, alkoxy, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $\text{NH}_2$ ,  $\text{NO}_2$ ,  $\text{CONH}_2$ , haloalkyl,  $\text{COOH}$ ,  $\text{COO-alkyl}$ ,  $-\text{OZ}'$ ,  $-\text{COOZ}'$ , a polyethylene glycol group, an alkyl sulfonate group, an alkyl- $\text{COOH}$  group, a substituted or unsubstituted benzyl group, a sugar derivative,  $-\text{C}\equiv\text{C}-(\text{CH}_2)_{p'}\text{CO}_2\text{R}_{12}$ , where  $\text{R}_{12}$  is H or alkyl, and  $\text{O}(\text{CH}_2)_{r'}\text{COR}_{13}$ , where  $\text{R}_{13}$  is OH, O-alkyl or N-succinimide, and  $p'$  and  $r'$  are each independently an integer from 1 to 10;

where  $Z$  and  $Z'$  are each independently silicon-containing protecting groups;

and wherein when  $a$ ,  $b$ ,  $c$  and  $d$  have the members necessary to complete a porphyrin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te,

- (a)  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are identical, and  $\text{R}_4 \neq \text{R}_1, \text{R}_2, \text{R}_3$ ; or
- (b)  $\text{R}_1 = \text{R}_3$ ;  $\text{R}_2 = \text{R}_4$ , where  $\text{R}_1, \text{R}_3 \neq \text{R}_2, \text{R}_4$ ; or
- (c)  $\text{R}_2 = \text{R}_3$ ;  $\text{R}_1 \neq \text{R}_4$ ; and  $\text{R}_1, \text{R}_4 \neq \text{R}_2, \text{R}_3$ .

## 2. A compound of formula Ia



wherein

one or two of A, B, C and D are each independently selected from S, O, Se and Te, and the remainder are N;

a, b, c and d are each independently substituted or unsubstituted 5-membered heterocyclic groups having the members necessary to complete a chlorin, bacteriochlorin or isobacteriochlorin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te;

M is H or a metal;

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each independently selected from:

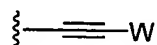
H;

alkyl;

cycloalkyl;

halogen;

aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, -OZ, -COOZ, a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative, -C≡C-(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>R<sub>10</sub>, where R<sub>10</sub> is H or alkyl, and O(CH<sub>2</sub>)<sub>r</sub>COR<sub>11</sub>, where R<sub>11</sub> is OH, O-alkyl or N-succinimide, and p and r are each independently an integer from 1 to 10;



wherein W is an aryl, alkyl or heteroaryl group, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, OZ', COOZ', a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative, -C≡C-(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>R<sub>12</sub>, where R<sub>12</sub> is

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H or alkyl, and  $O(CH_2)_rCOR_{13}$ , where  $R_{13}$  is OH, O-alkyl or N-succinimide, and  $p'$  and  $r'$  are each independently an integer from 1 to 10;  
 where Z and Z' are each independently silicon-containing protecting groups.

3. A compound according to claim 1 or claim 2 wherein one of A, B, C and D is S and the remainder are all N.

4. A compound according to any preceding claim wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently selected from:

H;

halogen;

phenyl or pyridyl, each of which are optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH, COO-alkyl, OZ, COOZ, a polyethylene glycol group,  $-C\equiv C-(CH_2)_pCO_2R_{10}$ , where  $R_{10}$  is H or alkyl, and  $O(CH_2)_rCOR_{11}$ , where  $R_{11}$  is OH, O-alkyl or N-succinimide, and p and r are each independently an integer from 1 to 10;

$\{ \text{---} \equiv \text{---} W$

wherein W is a phenyl or pyridyl group, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl, COOH, COO-alkyl, OZ', COOZ', a polyethylene glycol group,  $-C\equiv C-(CH_2)_pCO_2R_{12}$ , where  $R_{12}$  is H or alkyl, and  $O(CH_2)_rCOR_{13}$ , where  $R_{13}$  is OH, O-alkyl or N-succinimide, and  $p'$  and  $r'$  are each independently an integer from 1 to 10.

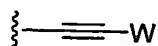
5. A compound according to any preceding claim wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently selected from:

H;

halogen;

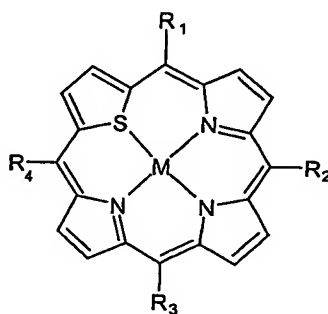
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phenyl or pyridyl, each of which are optionally substituted by one or more substituents selected from alkoxy, halogen, OH,  $\text{O}(\text{CH}_2)_r\text{COR}_{11}$  and  $-\text{C}\equiv\text{C}-(\text{CH}_2)_p\text{CO}_2\text{R}_{10}$ ;



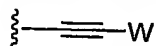
wherein W is phenyl or pyridyl, each of which may be optionally substituted by one or more substituents selected from OH, OZ' and a polyethylene glycol group.

6. A compound according to any one of claims 1, 3, 4 or 5 which is of formula II



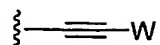
II

7. A compound according to claim 6 wherein  
 $\text{R}_1$  and  $\text{R}_4$  are different and are selected from aryl and heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $\text{CF}_3$ , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $\text{NH}_2$ ,  $\text{NO}_2$ ,  $\text{CONH}_2$ , haloalkyl,  $\text{COOH}$ ,  $\text{COO-alkyl}$ , OZ and  $\text{COOZ}$ ; and  
 $\text{R}_2$  and  $\text{R}_3$  are the same and are both H, halogen or



8. A compound according to claim 7 wherein  
 $\text{R}_1$  is aryl optionally substituted by an alkoxy group;  
 $\text{R}_2$  and  $\text{R}_3$  are both H, halogen or

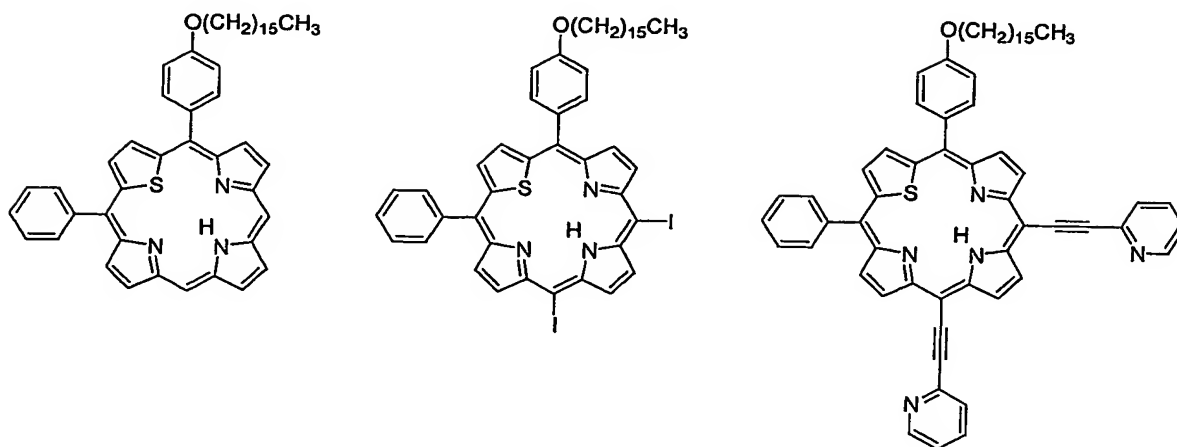
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where W is a pyridyl;

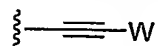
R<sub>4</sub> is phenyl.

9. A compound according to claim 8 which is selected from the following:



10. A compound according to claim 6 wherein

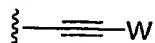
R<sub>1</sub> are R<sub>3</sub> are the same and are both H, halogen or



R<sub>2</sub> and R<sub>4</sub> are the same and are both aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, OZ and COOZ.

11. A compound according to claim 10 wherein

R<sub>1</sub> and R<sub>3</sub> are both H, halogen or

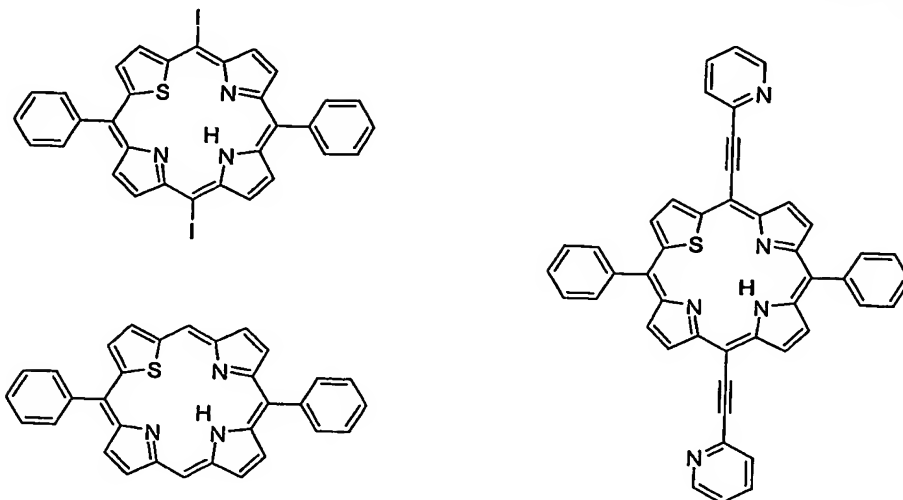


where W is pyridyl;

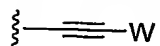
R<sub>2</sub> and R<sub>4</sub> are both phenyl.

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12. A compound according to claim 11 which is selected from the following:



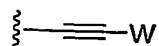
13. A compound according to claim 6 wherein  
 $R_1, R_2$  and  $R_3$  are the same and are all H, halogen or



$R_4$  is aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $\text{CF}_3$ , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $\text{NH}_2$ ,  $\text{NO}_2$ ,  $\text{CONH}_2$ , haloalkyl,  $\text{COOH}$ ,  $\text{COO-alkyl}$ ,  $\text{OZ}$ ,  $\text{COOZ}$ ,  $-\text{C}\equiv\text{C}-(\text{CH}_2)_p\text{CO}_2\text{R}_{10}$ , where  $\text{R}_{10}$  is H or alkyl, and  $\text{O}(\text{CH}_2)_r\text{COR}_{11}$ , where  $\text{R}_{11}$  is OH, O-alkyl or -N-succinimide, and  $p$  and  $r$  are each independently an integer from 1 to 10.

14. A compound according to claim 13 wherein

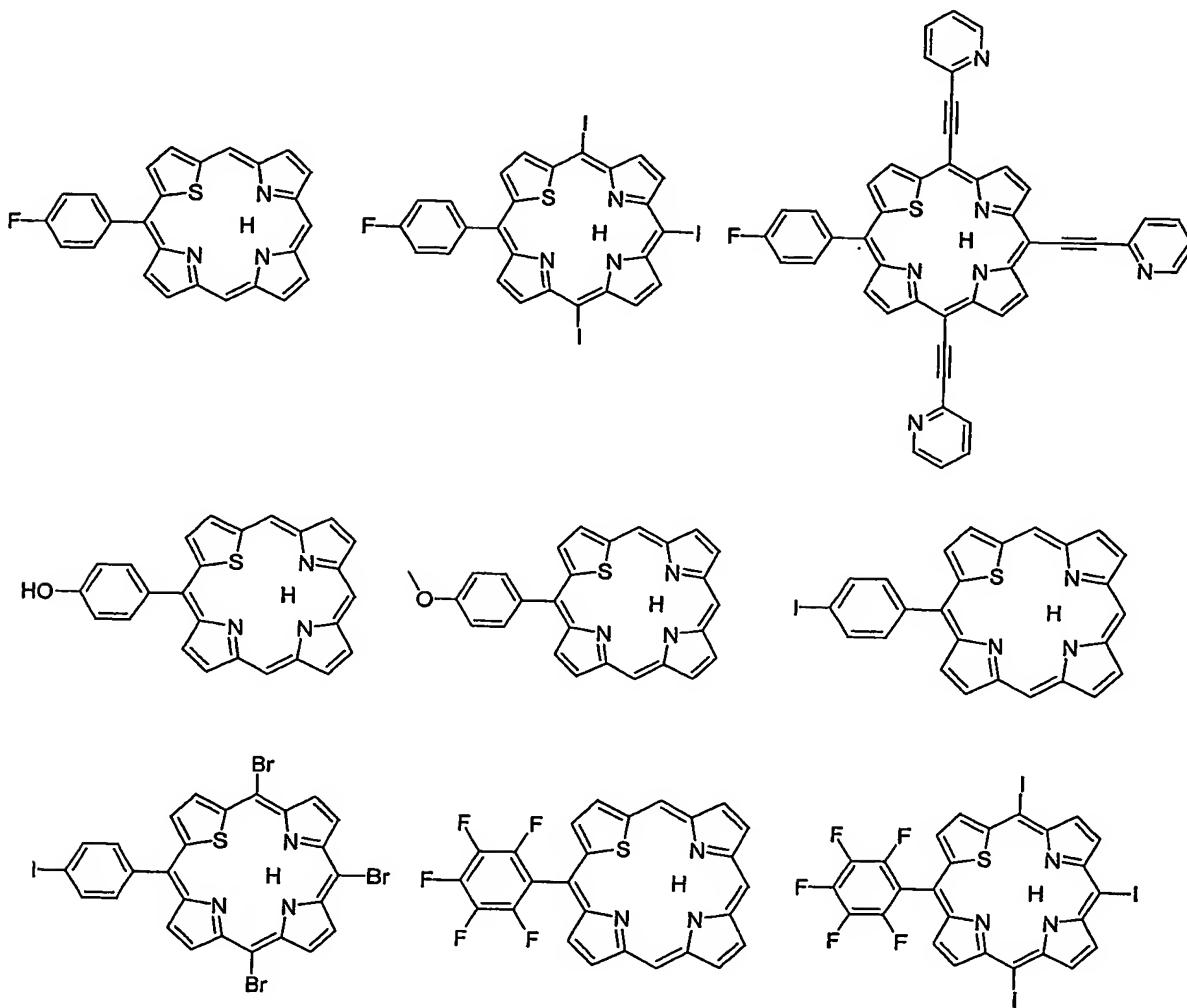
$R_1, R_2$  and  $R_3$  are all H, halogen or



where  $W$  is a pyridyl or phenyl group, each of which may be optionally substituted by one or more substituents selected from OH,  $\text{OZ}'$ , and a polyethylene glycol group; and  
 $R_4$  is a phenyl group substituted by one or more halogen, alkoxy,  $\text{O}(\text{CH}_2)_p\text{COR}_{11}$  or  $-\text{C}\equiv\text{C}-(\text{CH}_2)_p\text{CO}_2\text{R}_{10}$  groups.

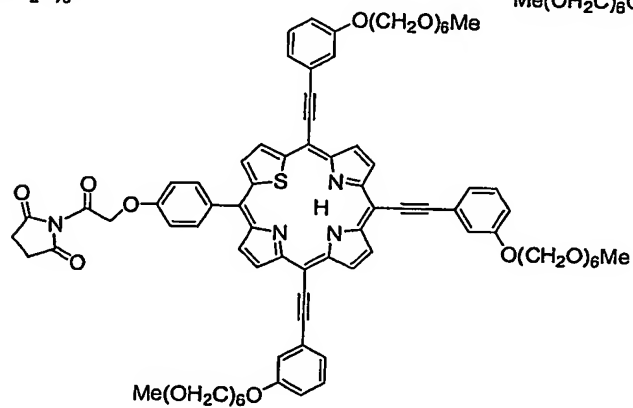
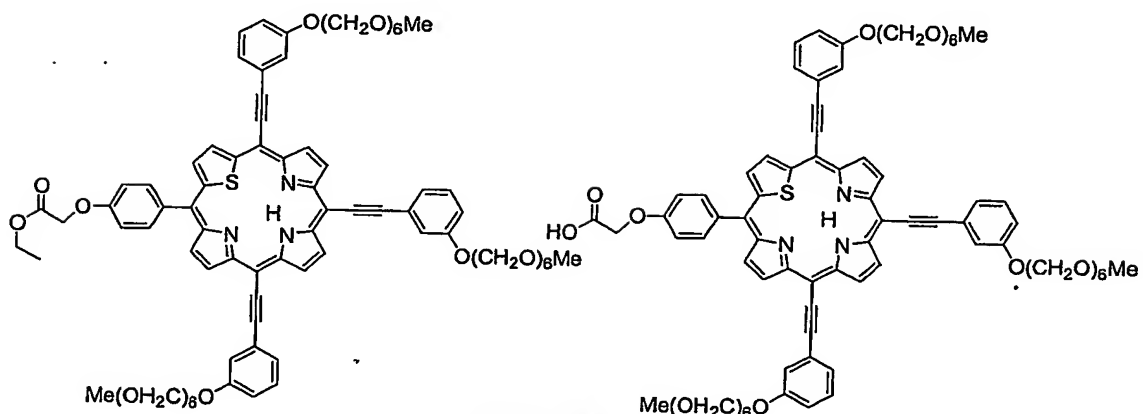
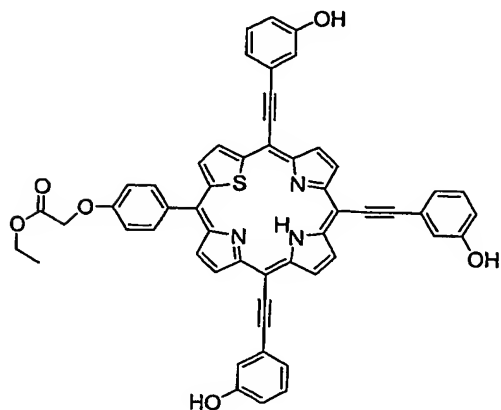
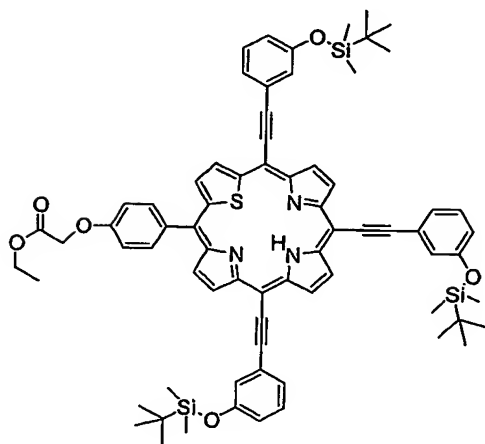
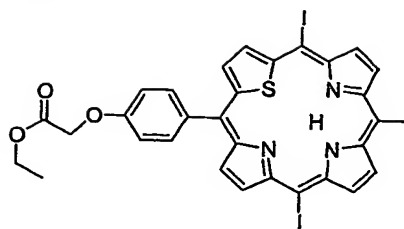
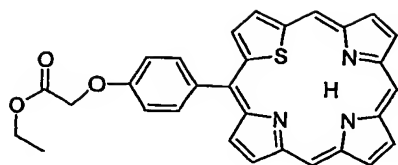
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15. A compound according to claim 14 wherein said compound is selected from the following:

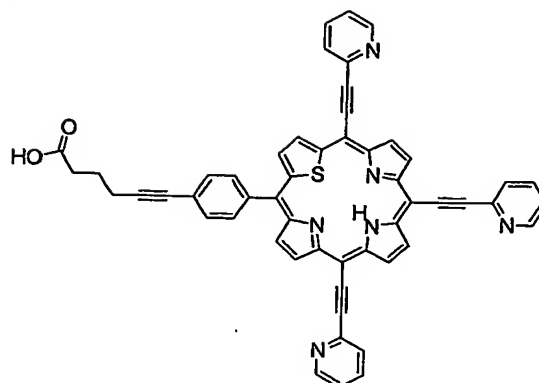
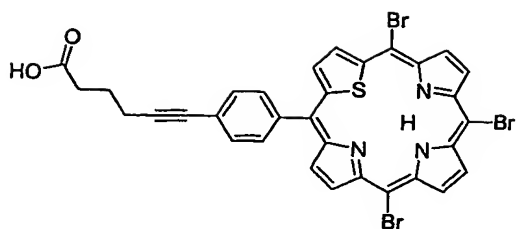




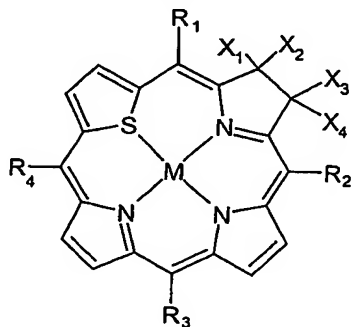
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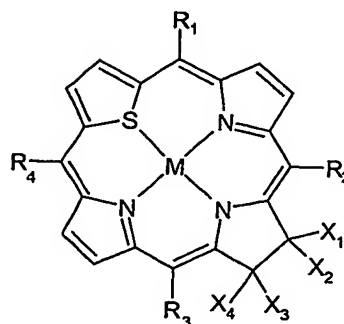
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16. A compound according to any one of claims 1 to 5 which is of formula III or IV



III

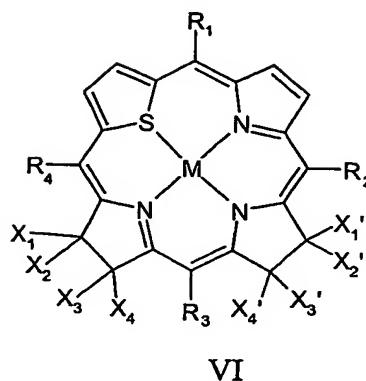
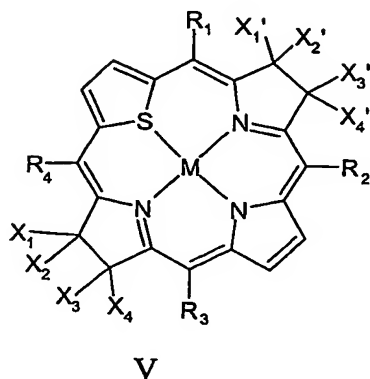


IV

wherein  $\text{X}_1$ - $\text{X}_4$  are each independently selected from H, OH, alkyl, alkoxy; or  $\text{C}=\text{O}$ , where  $\text{X}_2$  and  $\text{X}_4$  respectively are absent, and  $\text{R}_1$ - $\text{R}_4$  and M are as defined in claim 1.

17. A compound according to claim 16 wherein  $\text{X}_1$  and  $\text{X}_3$  are OH, and  $\text{X}_2$  and  $\text{X}_4$  are H.

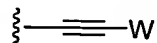
18. A compound according to any one of claims 1 to 5 which is of formula V or VI



wherein  $R_1$ - $R_4$  and  $M$  are as defined in claim 1, and  $X_1$ - $X_4$  and  $X_1'$ - $X_4'$  are each independently selected from H, OH, alkyl, alkoxy; or C=O, where  $X_2$ ,  $X_4$ ,  $X_2'$  and  $X_4'$  respectively are absent.

19. A compound according to claim 18 wherein  $X_1$ ,  $X_3$ ,  $X_1'$  and  $X_3'$  are OH, and  $X_2$ ,  $X_4$ ,  $X_2'$  and  $X_4'$  are all H.

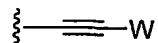
20. A compound according to claim 16 or claim 18 wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same and are all H, halogen or



$R_4$  is aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $\text{CF}_3$ , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $\text{NH}_2$ ,  $\text{NO}_2$ ,  $\text{CONH}_2$ , haloalkyl, COOH, COO-alkyl, OZ and COOZ.

21. A compound according to claim 20 wherein

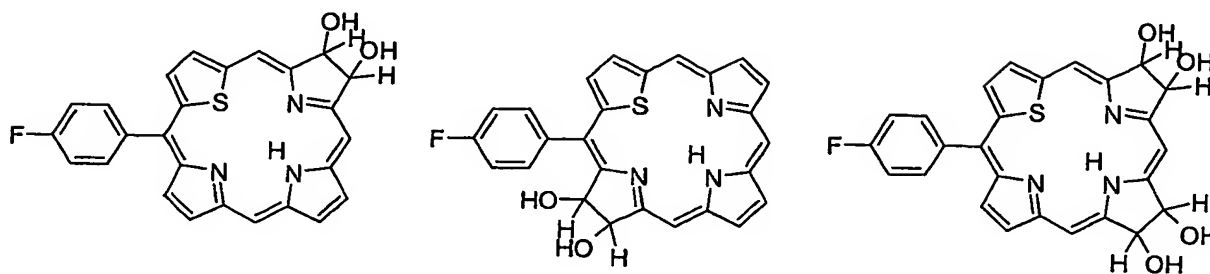
$R_1$ ,  $R_2$  and  $R_3$  are all H, halogen or



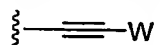
where  $W$  is pyridyl; and

R<sub>4</sub> is a halogen substituted aryl group.

22. A compound according to claim 21 which is selected from:

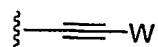


23. A compound according to claim 16 or claim 18 wherein  
R<sub>2</sub> and R<sub>3</sub> are the same and are both H, halogen or



R<sub>1</sub> and R<sub>4</sub> are different and are aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF<sub>3</sub>, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH<sub>2</sub>, NO<sub>2</sub>, CONH<sub>2</sub>, haloalkyl, COOH, COO-alkyl, OZ and COOZ.

24. A compound according to claim 23 wherein  
R<sub>2</sub> and R<sub>3</sub> are both H, halogen or

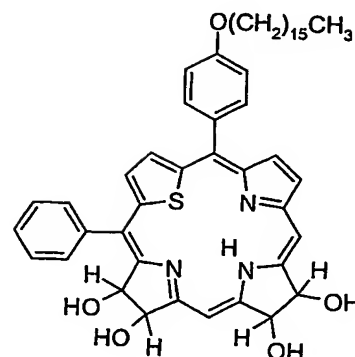
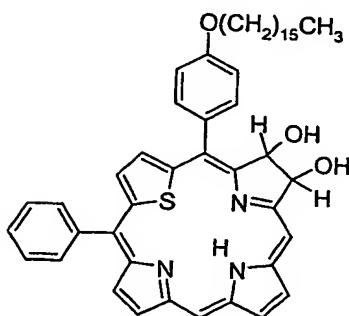
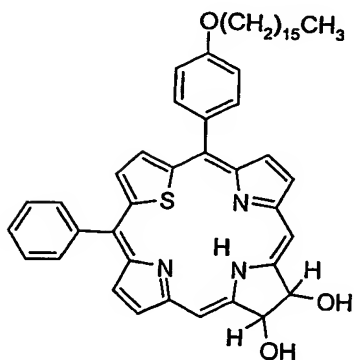


where W is pyridyl;

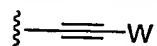
R<sub>4</sub> is phenyl; and

R<sub>1</sub> is alkoxy substituted phenyl.

25. A compound according to claim 24 which is selected from:



26. A compound according to claim 16 or claim 18 wherein  
 $R_1$  and  $R_3$  are the same and are both aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN,  $CF_3$ , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide,  $NH_2$ ,  $NO_2$ ,  $CONH_2$ , haloalkyl,  $COOH$ ,  $COO$ -alkyl, OZ and  $COOZ$ ; and  
 $R_2$  and  $R_4$  are the same and are both H, halogen or



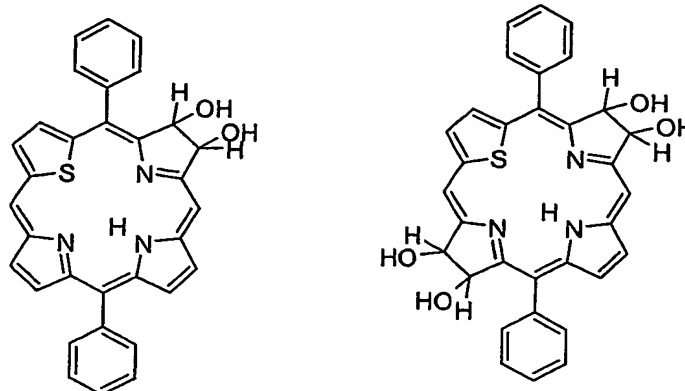
27. A compound according to claim 26 wherein

$R_1$  and  $R_3$  are both phenyl; and

$R_2$  and  $R_4$  are both H.

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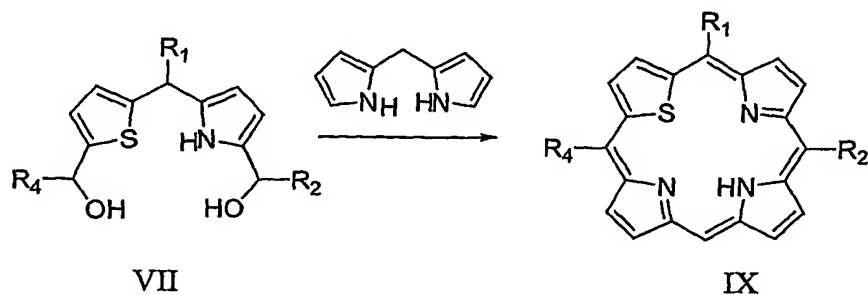
28. A compound according to claim 27 which is selected from the following:



29. A compound according to any preceding claim wherein M is selected from H, Ni, Pb, V, Pd, Co, Nb, Al, Sn, Zn, Cu, Mg, Ca, In, Ga, Fe, Eu, Lu, Pt, Ru, Mn and Ge.
30. A compound according to any preceding claim wherein M is H or Zn.
31. A pharmaceutical composition comprising a compound according to any one of claims 1 to 30 admixed with a pharmaceutically acceptable diluent, excipient or carrier.
32. A conjugate molecule comprising a compound as defined in any one of claims 1 to 30 and a targeting moiety selected from a recombinant antibody, a Fab fragment, a F(ab')<sub>2</sub> fragment, a single chain Fv, a diabody, a disulfide linked Fv, a single antibody domain and a CDR.
33. A conjugate molecule which comprises a polypeptide carrier comprising at least one alpha helix having synthetically attached thereto a plurality of compounds as defined in any one of claims 1 to 30.
34. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33 in medicine.

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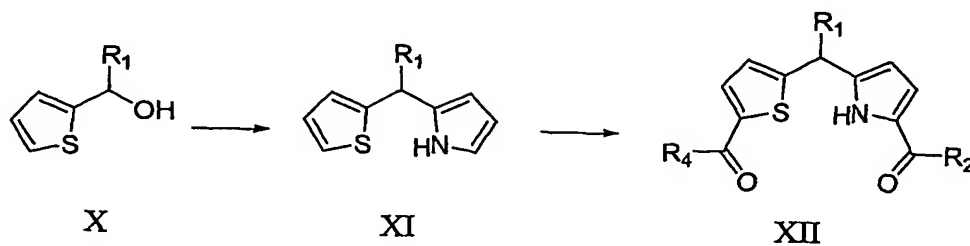
35. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, for medical imaging.
36. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, in the preparation of a medicament for photodynamic therapy.
37. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, in the preparation of a medicament for treating a proliferative disorder.
38. Use of a compound according to any one of claims 1 to 30 in the preparation of a conjugate according to claim 32 or claim 33.
39. A method of treating a proliferative disorder, said method comprising administering to a subject a therapeutic amount of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33.
40. A process for preparing a compound as defined in claim 1 or claim 2, said process comprising reacting a compound of formula VII with a dipyrrole to form a compound of formula IX



where R<sub>1</sub>, R<sub>2</sub> and R<sub>4</sub> are as defined in claim 1.

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41. A process according to claim 40 wherein said compound of formula VII is prepared via intermediates X, XI and XII



42. A process according to claim 40 or claim 41 for preparing a compound according to claim 17 or claim 19 which further comprises oxidising said compound of formula IX with osmium tetroxide.